Review of Matrices

☞ A matrix is a rectangular array of numbers that combines with other such arrays according to specific rules.

$$\begin{bmatrix} a_{11} & a_{12} & \ldots & a_{1n} \\ a_{21} & a_{22} & \ldots & a_{2n} \\ . & . & \ldots & . \\ . & . & \ldots & . \\ . & . & \ldots & . \\ a_{m1} & a_{m2} & \ldots & a_{mn} \end{bmatrix}$$

✓ The dimension of a matrix is given as rows x columns; i.e., m x n.

Matrix Multiplication

☞ If two matrices are to be multiplied together they must be *conformable*; i.e., the number of columns in the first (left) matrix must be the same as the number of rows in the second (right) matrix.

✓ The product matrix has as many rows as the first matrix and as many columns as the second matrix.

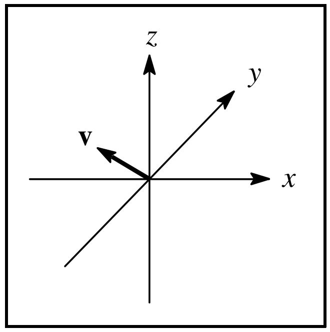
$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}$$

✓ The elements of the product matrix, c_{ij}, are the sums of the products $a_{ik}b_{kj}$ for all values of k from 1 to m; i.e.,

$$c_{ij} = \sum_{k=1}^{m} a_{ik} b_{kj}$$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix} = \begin{bmatrix} (a_{11}b_{11} + a_{12}b_{21}) & (a_{11}b_{12} + a_{12}b_{22}) & (a_{11}b_{13} + a_{12}b_{23}) \\ (a_{21}b_{11} + a_{22}b_{21}) & (a_{21}b_{12} + a_{22}b_{22}) & (a_{21}b_{13} + a_{22}b_{23}) \\ (a_{31}b_{11} + a_{32}b_{21}) & (a_{31}b_{12} + a_{32}b_{22}) & (a_{31}b_{13} + a_{32}b_{23}) \end{bmatrix}$$

Transformations of a General Vector in C_{2v}



E

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

C_2

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$\sigma_v = \sigma_{xz}$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

$\sigma_v' = \sigma_{yz}$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

A Representation with Matrices

C_{2v}	E	C_2	σ_v	σ_v'
Γ_m	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

✓ These matrices combine with each other in the same ways as the operations, so they form a representation of the group.

✓ Γ_m is a **reducible representation**

☞ The *character* of a matrix (symbol chi, χ) is the sum of the elements along the left-to-right diagonal (the *trace*) of the matrix.

$\chi(E) = 3$ $\quad$ $\chi(C_2) = -1$ $\quad$ $\chi(\sigma_v) = 1$ $\quad$ $\chi(\sigma_v') = 1$

☞ A more compact form of a reducible representation can be formed by using the characters of the full-matrix form of the representation.

✓ We will most often use this form of representation.

✓ The character form of a representation does not by itself conform to the multiplication table of the group; only the original matrix form does this.

A Representation from the Traces (Characters) of the Matrices

C_{2v}	E	C_2	σ_v	σ_v'
Γ_v	3	-1	1	1

✓ The characters of Γ_v are the sums of the corresponding characters of the three irreducible representations $A_1 + B_1 + B_2$:

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ_v	3	-1	1	1

✎ $\Gamma_v = A_1 + B_1 + B_2$

✓ Breaking down Γ_v into its component irreducible representations is called **reduction**.

✓ The species into which Γ_v reduces are the those by which the vectors **z**, **x**, and **y** transform, respectively.

Reduction of Γ_m by Block Diagonalization

C_{2v}	E			C_2			σ_v			σ_v'			
	1	0	0	-1	0	0	1	0	0	-1	0	0	B_1
Γ_m	0	1	0	0	-1	0	0	-1	0	0	1	0	B_2
	0	0	1	0	0	1	0	0	1	0	0	1	A_1

✓ Each diagonal element, c_{ii}, of each operator matrix expresses how one of the coordinates x, y, or z is transformed by the operation.

- ➜ Each c_{11} element expresses the transformation of the x coordinate.
- ➜ Each c_{22} element expresses the transformation of the y coordinate.
- ➜ Each c_{33} element expresses the transformation of the z coordinate.

✓ The set of four c_{ii} elements with the same i (across a row) is an irreducible representation.

✓ The three irreducible representations found by block diagonalization of Γ_m are the same as those found for Γ_v; i.e.,

$$\Gamma_m = A_1 + B_1 + B_2 = \Gamma_v$$

☞ The reduction of a reducible representation in either full-matrix or character form gives the same set of component irreducible representations.

Dimensions of Representations

☞ In a representation of matrices, such as Γ_m, the *dimension of the representation* is the order of the square matrices of which it is composed.

$$d\,(\Gamma_m) = 3$$

☞ For a representation of characters, such as Γ_v, the dimension is the value of the character for the identity operation.

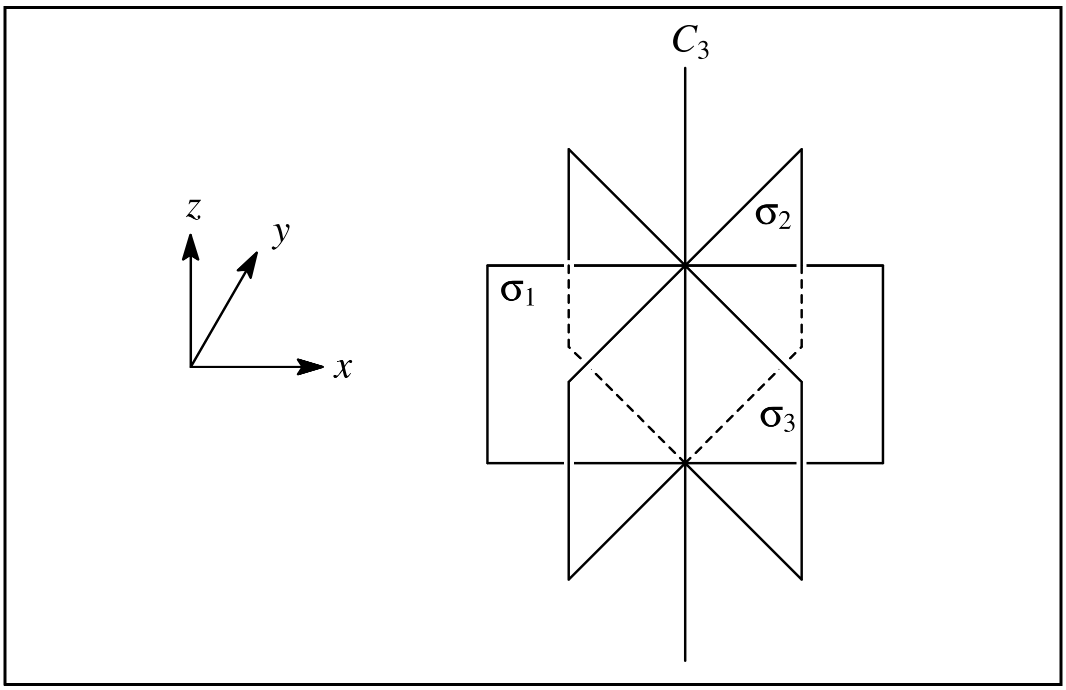
$$\chi(E) = 3 \quad \Rightarrow \quad d\,(\Gamma_v) = 3$$

☞ The dimension of the reducible representation must equal the sum of the dimensions of all the irreducible representations of which it is composed.

$$d_r = \sum_i n_i d_i$$

More Complex Groups and Standard Character Tables

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	$(x^2-y^2, xy)(xz, yz)$



☞ The group C_{3v} has:

- ✓ Three classes of elements (symmetry operations).
- ✓ Three irreducible representations.
- ✓ One irreducible representation has a dimension of $d_i = 2$ (*doubly degenerate*).

☞ The character table has a last column for *direct product transformations.*

Classes

☞ **Geometrical Definition** (Symmetry Groups): Operations in the same class can be converted into one another by changing the axis system through application of some symmetry operation of the group.

☞ **Mathematical Definition** (All Groups): The elements A and B belong to the same class if there is an element X within the group such that $X^{-1}AX = B$, where X^{-1} is the inverse of X (i.e., $XX^{-1} = X^{-1}X = E$).

- ✓ If $X^{-1}AX = B$, we say that B is the s*imilarity transform* of A by X, or that A and B are *conjugate* to one another.

- ✓ The element X may in some cases be the same as either A or B.

Classes of C_{3v} by Similarity Transforms

C_{3v}	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

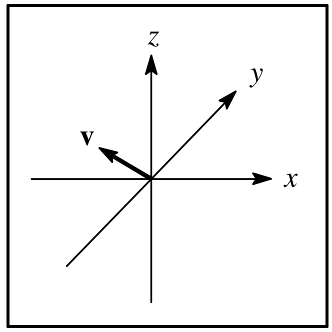
☞ Take the similarity transforms on C_3 to find all members in its class:

$EC_3E = C_3$
$C_3^2C_3C_3 = C_3^2C_3^2 = C_3$
$C_3C_3C_3^2 = C_3E = C_3$
$\sigma_1C_3\sigma_1 = \sigma_1\sigma_3 = C_3^2$
$\sigma_2C_3\sigma_2 = \sigma_2\sigma_1 = C_3^2$
$\sigma_3C_3\sigma_3 = \sigma_3\sigma_2 = C_3^2$ ✓ Only C_3 and C_3^2

☞ Take the similarity transforms on σ_1 to find all members in its class:

$E\,\sigma_1E = \sigma_1$
$C_3^2\,\sigma_1C_3 = C_3^2\,\sigma_2 = \sigma_3$
$C_3\,\sigma_1C_3^2 = C_3\,\sigma_3 = \sigma_2$
$\sigma_1\,\sigma_1\,\sigma_1 = \sigma_1E = \sigma_1$
$\sigma_2\,\sigma_1\,\sigma_2 = \sigma_1\,C_3 = \sigma_2$
$\sigma_3\,\sigma_1\,\sigma_3 = \sigma_1C_3^2 = \sigma_3$ ✓ Only σ_1, σ_2, and σ_3

Transformations of a General Vector in C_{3v}
The Need for a Doubly Degenerate Representation



- ☞ No operation of C_{3v} changes the z coordinate.

  - ✓ Every operation involves an equation of the form

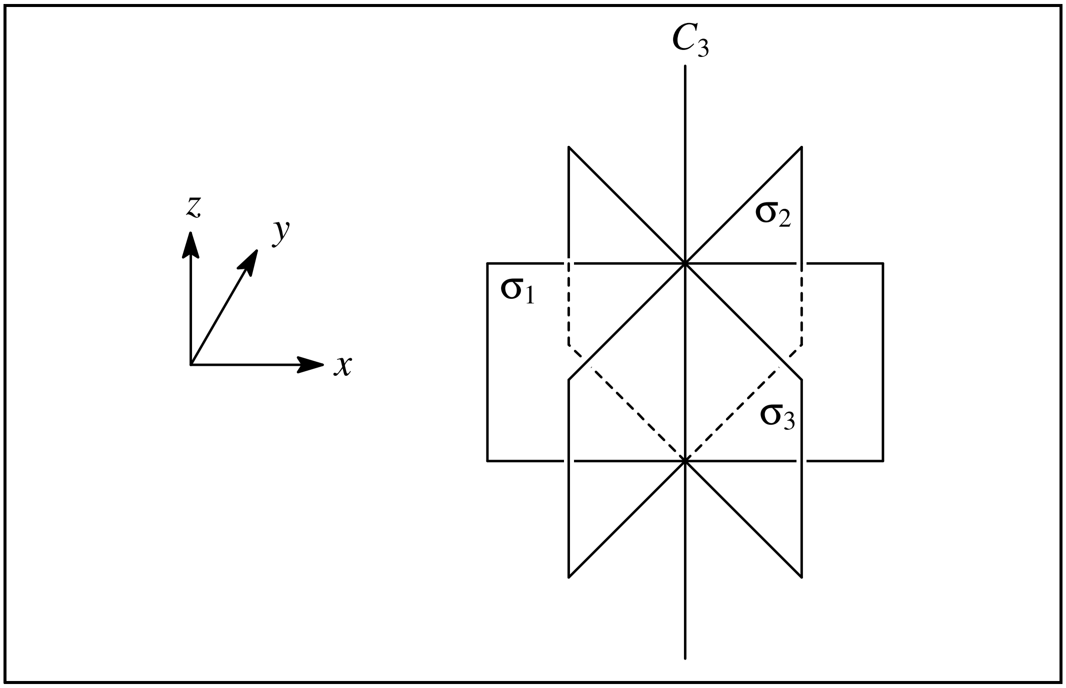
$$\begin{bmatrix} ? & ? & 0 \\ ? & ? & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} ? \\ ? \\ z \end{bmatrix}$$

  - ✓ We only need to describe any changes in the projection of **v** in the *xy* plane.

- ☞ The operator matrix for each operation is generally unique, but all operations in the same class have the same character from their operator matrices.

  - ✓ We only need to examine the effect of one operation in each class.

Transformations by E and $\sigma_1 = \sigma_{xz}$



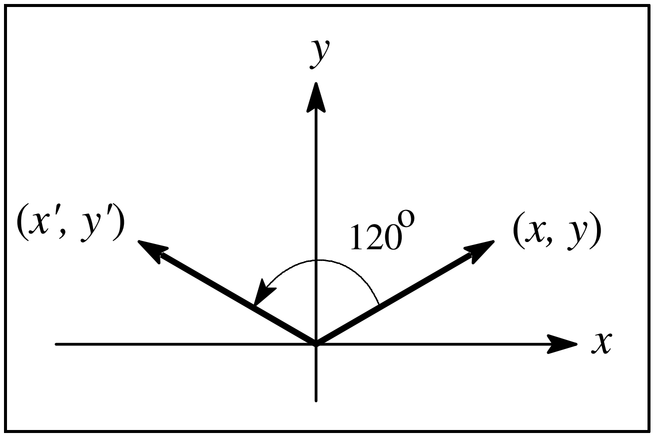
E

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$\sigma_1 = \sigma_{xz}$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

Transformation by C_3



From trigonometry:

$$x' = \cos\frac{2\pi}{3}x - \sin\frac{2\pi}{3}y = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y$$

$$y' = \sin\frac{2\pi}{3}x + \cos\frac{2\pi}{3}y = \frac{\sqrt{3}}{2}x - \frac{1}{2}y$$

Therefore, the transformation matrix has nonzero off-diagonal elements:

$$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \left(-\frac{x}{2} - \frac{\sqrt{3}y}{2}\right) \\ \left(\frac{\sqrt{3}x}{2} - \frac{y}{2}\right) \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

Reduction by Block Diagonalization

$$
\begin{array}{c|ccc}
C_{3v} & E & C_3 & \sigma_v \\
\hline
\Gamma_m &
\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & \boxed{1} \end{array} &
\begin{array}{cc|c} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ \hline 0 & 0 & \boxed{1} \end{array} &
\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & \boxed{1} \end{array}
\end{array}
$$

☞ The blocks must be the same size across all three matrices.

✓ The presence of nonzero, off-diagonal elements in the transformation matrix for C_3 restricts us to diagonalization into a 2x2 block and a 1x1 block.

✓ For all three matrices we must adopt a scheme of block diagonalization that yields one set of 2x2 matrices and another set of 1x1 matrices.

Representations of Characters

☞ Converting to representations of characters gives a doubly degenerate irreducible representation and a nondegenerate representation.

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma_{x,y} = E$	2	-1	0
$\Gamma_z = A_1$	1	1	1

✓ Any property that transforms as E in C_{3v} will have a companion, with which it is degenerate, that will be symmetrically and energetically equivalent.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	$(x^2-y^2, xy)(xz, yz)$

✓ Unit vectors **x** and **y** are degenerate in C_{3v}.

✓ Rotational vectors $\boldsymbol{R_x}$, $\boldsymbol{R_y}$ are degenerate in C_{3v}.

Direct Product Listings

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	$(x^2 - y^2, xy)(xz, yz)$

☞ The last column of typical character tables gives the transformation properties of direct products of vectors.

✓ Among other things, these can be associated with the transformation properties of *d* orbitals in the point group.

Correspond to *d* orbitals: z^2, $x^2 - y^2$, xy, xz, yz, $2z^2 - x^2 - y^2$

Do not correspond to *d* orbitals: x^2, y^2, $x^2 + y^2$, $x^2 + y^2 + z^2$

Complex-Conjugate Paired Irreducible Representations

☞ Some groups have irreducible representations with imaginary characters in complex conjugate pairs:

$$C_n\ (n \geq 3),\ C_{nh}\ (n \geq 3),\ S_{2n},\ T,\ T_h$$

- ✓ The paired representations appear on successive lines in the character tables, joined by braces ({ }).
- ✓ Each pair is given the single Mulliken symbol of a doubly degenerate representation (e.g., E, E_1, E_2, E', E'', E_g, E_u).
- ✓ Each of the paired complex-conjugate representations is an irreducible representation in its own right.

Combining Complex-Conjugate Paired Representations

☞ It is sometimes convenient to add the two complex-conjugate representations to obtain a representation of real characters.

✓ When the pair has ε and ε* characters, where $\varepsilon = \exp(2\pi i/n)$, the following identities are used in taking the sum:

$$\varepsilon^p = \exp(2\pi pi/n) = \cos 2\pi p/n + i\sin 2\pi p/n$$

$$\varepsilon^{*p} = \exp(-2\pi pi/n) = \cos 2\pi p/n - i\sin 2\pi p/n$$

which combine to give

$$\varepsilon^p + \varepsilon^{*p} = 2\cos 2\pi p/n$$

Example: In C_3, $\varepsilon = \exp(2\pi i/3) = \cos 2\pi/3 - i\sin 2\pi/3$ and $\varepsilon + \varepsilon^* = 2\cos 2\pi/3$.

C_3	E	C_3	C_3^2
E^a	1	ε	ε^*
E^b	1	ε^*	ε
$\{E\}$	2	$2\cos 2\pi/3$	$2\cos 2\pi/3$

☞ If complex-conjugate paired representations are combined in this way, realize that the real-number representation is a *reducible* representation.

Mulliken Symbols
Irreducible Representation Symbols

In non-linear groups:

A	nondegenerate; symmetric to C_n ($\chi_{C_n} > 0$)
B	nondegenerate; antisymmetric to C_n ($\chi_{C_n} < 0$)
E	doubly degenerate ($\chi_E = 2$)
T	triply degenerate ($\chi_E = 3$)
G	four-fold degenerate ($\chi_E = 4$) in groups I and I_h
H	five-fold degenerate ($\chi_E = 5$) in groups I and I_h

In linear groups $C_{\infty v}$ and $D_{\infty h}$:

$\Sigma \equiv A$	nondegenerate; symmetric to C_∞ ($\chi_{C_\infty} = 1$)
$\{\Pi, \Delta, \Phi\} \equiv E$	doubly degenerate ($\chi_E = 2$)

Mulliken Symbols
Modifying Symbols

With any degeneracy in any centrosymmetric groups:

subscript *g*	(*gerade*) symmetric with respect to inversion ($\chi_i > 0$)
subscript *u*	(*ungerade*) antisymmetric with respect to inversion ($\chi_i < 0$)

With any degeneracy in non-centrosymmetric nonlinear groups:

prime (')	symmetric with respect to σ_h ($\chi_{\sigma_h} > 0$)
double prime (")	antisymmetric with respect to σ_h ($\chi_{\sigma_h} < 0$)

With nondegenerate representations in nonlinear groups:

subscript 1	symmetric with respect to C_m ($m < n$) or σ_v ($\chi_{C_m} > 0$ or $\chi_{\sigma_v} > 0$)
subscript 2	antisymmetric with respect to C_m ($m < n$) or σ_v ($\chi_{C_m} < 0$ or $\chi_{\sigma_v} < 0$)

With nondegenerate representations in linear groups ($C_{\infty v}$, $D_{\infty h}$):

superscript +	symmetric with respect to $\infty\sigma_v$ or ∞C_2 ($\chi_{\sigma_v} = 1$ or $\chi_{C_2} = 1$)
superscript –	antisymmetric with respect to $\infty\sigma_v$ or ∞C_2 ($\chi_{\sigma_v} = -1$ or $\chi_{C_2} = -1$)